

## INFLUENCE OF HIGHWAY DISTANCE ON HEAVY METALS DYNAMICS IN THE SOIL-FRUIT SYSTEM

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### **Abstract**

At five locations of apple orchards grown on eutric cambisol at a different distance from the E 75 highway, the presence of heavy metals in soil and plant material was examined. In the soil samples it were determined pH in 1M KCl, CaCO<sub>3</sub>, total C, SOM, content of clay and content of total and available forms of Cu, Ni, Pb and Zn. Content of Cu, Ni, Pb and Zn was analyzed in the plant material. In the tested soil samples, the content of the total forms of the tested elements is within the limits of maximum allowable concentrations, while in the tested plant material, only the content of lead in one of the five tested apple samples is within the permitted limits. In apple samples from locations 30 m away from the highway, the lead content is well above the limit values, which requires further research to determine whether the increased concentration of this element is due to aerosol pollution or protective equipment applied.

**Key words:** Highway, soil, apple, heavy metals

### **Introduction**

Metals are the main inorganic pollutants related to traffic. Common source of soil and plant contamination with heavy metals is traffic [8]. Metals are also found in road dust, emitted by vehicles, particles from the deterioration of the track pavement, industrial activities, and naturally from the soil minerals [7, 20]. Fast development of industry, continuously increasing population, and intensification of road traffic are regarded as the foremost causes of ecosystem pollution in urban areas [9]. Cr and Ni are more associated with the corrosion of vehicles and their chrome parts [3]. Numerous studies on roadside soil pollution have focused on total emission loads of heavy metals into open grassland and agricultural areas [18]. Generally, total heavy metal contents in roadside soils were found strongly dependent on traffic density and showed an exponential decrease with distance from the road, reaching background levels 10-100 meters. The most frequently reported heavy metals of concern have been Pb, Zn and Cu. Among the contaminants that are transferred to plant tissue are Cd, Cr, Cu, Ni, Pb, Zn and their uptake depends on their concentration in the soil solution, which in turn is affected by the level and form of metal present and soil pH. In general, the solubility and uptake of metals are less at higher soil pH [12]. The mobility of the trace elements and their translocation in the plant are influenced by the content of the clay fraction, organic matter and pH value of soil [4]. Plants are the intermediaries through which elements from the soil and partly from the air and water are transferred to the human body by consumption. Some of the elements are necessary for growth and development of crops and without them they cannot survive, some of them have stimulating effect on plant growth, while a group of elements at high concentrations affects very toxically on the plants [18]. Concentrations of metals in plants vary with plant species [1]. Plant uptake of heavy metals from soil occurs either passively with the mass flow of water into the roots, or through active transport crosses the plasma membrane of root epidermal cells [13]. Heavy metals are naturally present in the environment, however, the dynamic development of industry and motorization, as well as the

continuing over-intensive use of various chemical compounds in agriculture, causes constantly increase of toxic heavy metals in the environment [2].

### Material and Methods

Sampling of soil samples to a depth of 30 cm and apples from the orchard was performed in orchard established on soil type Eutric Cambisol [19], at a distance of 30, 50 and 400 meters from the highway lane E 75 during August and September 2010, as part of research within the project "Investigation of the presence of dangerous and harmful substances in agricultural soil on the most important crop and vegetable crops in the E 75 highway zone", which covered the entire section of the above mentioned highway. Table 1 presents the coordinates of the sampling locations and the distance from the highway lanes.

Table 1.-List of locations of samples and type of soil

Study site	(m from route lanes)	Coordinate	
		X	Y
1	D(30)	7475052	4935866
2	D(50)	7475069	4935835
3	D(30)	7490188	4937435
4	D(50)	7490165	4937420
5	D(400)	7490042	4937222

### Soil analysis

In the laboratory, composite soil samples were dried and passed through a 2-mm sieve. Soil pH in water and in 1M KCl was analyzed potentiometrically, using glass electrode (SRPS ISO 10390:2007); calcium carbonate by volumetric method SRPS ISO 10693: 2005- Determination of carbonate content; total contents C was analyzed on elemental CNS analyzer Vario EL III [16]. SOM (soil organic matter) was calculated using the formula: SOM content (%) = organic C content (%) x factor 1.724 in carbonless soil samples, ie SOM content (%) = (organic C content (%) - 0.12 x% CaCO<sub>3</sub>) x factor 1.724 for carbonate soil samples [5]; granulometric composition was analyzed by standardized method by sieving and sedimentation (ISO 11277: 2009(E), 2009). Determination of trace elements in ICP-AES soil extracts was analyzed by standardized method ISO 22036: 2008; Available forms of Ni, Pb, Cu, Zn - DTPA buffer solution extraction and determination by ICP using method: SRPS ISO 14870: 2005. Reference soil NCS ZC 73005 (Soil Certificate of Certified Reference Materials approved by China National Analysis Center Beijing China) and reagent blanks were used as the quality assurance and quality control (QA/QC) samples during the analysis.

### Plant analysis

Analyzed aerial parts of the study plant species were dried for 2 hours at 105°C, using gravimetric method for determination of dry matter content of plant tissue. The dry matter determination is used to correct the sample element concentration to an absolute dry matter basis [15]. The content of heavy metals in selected plants was determined with an inductively coupled plasma optical emission spectrometer ICAP 630 (ICP-OES), after the samples were digested with concentrated HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> for total form extraction.

### Results and discussion

Soil suitable for the production of health safe food should not contain dangerous and harmful substances, so it is very important to know their content and distribution. High concentrations of heavy metals in soil pose a significant risk to the agro-ecosystem because of their persistancy and, when incorporated in to the soil, remain present for many years, building

strong links with soil components. The origin and content of heavy metals is primarily of geochemical origin, but also due to atmospheric deposition as is the case on soil adjacent to roads. Likewise, one of the causes of the increased content of heavy metals may be of anthropogenic character by the application of fertilizers and pesticides containing increased concentrations of heavy metals that accumulate in it. The land on which the apple plantations are based belongs to the type Eutric Cambisol [19]. The obtained values of the content of the studied Physical and chemical properties of tested soil samples and microelements and heavy metals are shown in Table 2 and 3.

Table 2. Physical and chemical properties of tested soil samples

Study site	Clay fraction (<0.002 mm) %	pH 1M KCl	C (%)	CaCO <sub>3</sub> (%)	SOM (%)
1	12.1	6.10	3.11	0.41	5.27
2	11.3	4.40	1.90	BLMD	3.27
3	7.8	6.30	2.03	BLMD	3.50
4	8.2	6.20	1.99	BLMD	3.43
5	7.5	3.60	2.35	BLMD	4.05

SOM-soil organic matter; BLMD-below the limit of the method detection

Table 3. The content of total and available forms trace elements in soil samples

Study site	Soil total forms				Soil available forms			
	Cu	Ni	Pb	Zn	Cu	Ni	Pb	Zn
	(mg kg <sup>-1</sup> )							
1	19.62	34.19	34.84	80.31	2.50	1.10	2.12	4.65
2	28.82	34.68	32.60	71.91	7.80	2.39	3.09	7.12
3	23.85	48.20	50.60	73.76	4.20	2.32	1.86	4.38
4	23.68	49.74	29.83	66.66	4.10	2.64	1.55	4.64
5	38.05	41.12	32.58	80.21	11.40	3.00	3.50	6.12

The interpretation of data on the trace elements content in soil samples was done according to the Rule book of maximum permissible levels (MPL) of dangerous and hazardous materials in soil and water for irrigation and methods for analysis [17], where MPL for Cu is 100 mg kg<sup>-1</sup>, MLP for Zn is 300 mg kg<sup>-1</sup>, MPL for Ni is 50 mg kg<sup>-1</sup> and MLP for Pb is 100 mg kg<sup>-1</sup>.

The interpretation of the results of the heavy metal content in the tested apple fruit was based on additional literature sources were used for data analysis: recommendations of the World Health Organisation on maximum allowable concentrations of heavy metals in fruits and vegetables [6] and scientific literature [14,10,11], Table 4.

Table 4. Average and toxic concentration of heavy metals in plants

Element	Limit values WHO	Normal content in plants Kloeke et al. *	Critical contents for plant food Kloeke et al. *	Critical concentration Kastori et al.**	Toxical concentration Kastori et al.**
(mg kg <sup>-1</sup> )					
Cu	0.3	3-15	15-20	15	20
Ni		0.1-5	20-30	20	30
Pb			0.1-0.2	0.1	0.2
Zn		15-150	150-200	150	200

Table 5. shows the percentages of examined Cu, Ni, Pb and Zn in the fresh matter of the apple fruit by test locations.

Table 5. The content of the tested elements in the apple fruit calculated on fresh matter

Location	1	2	3	4	5
Element	(mg kg <sup>-1</sup> ) fresh matter				
Cu	1,38	0,99	1,31	0,98	1,04
Ni	0,7	0,77	0,29	0,26	1,78
Pb	<b>1,64</b>	0,28	<b>1,49</b>	0,19	0,26
Zn	8,98	14,55	12,63	8,38	9,01

The obtained results indicate that the content of the tested elements above the MPC was not detected in the tested soil samples. In the samples of apple fruits only in sample 4, the content of Pb is within the allowed limits, therefore, further investigations would require a more detailed examination of the possible impact of aerial contamination and contamination of the fruits due to the use of plant protection products. In samples 1 and 3, the lead content is well above the limit value, and since it was sampled at a distance of 30 m from the highway, it is assumed that the the main cause of contamination is motor vehicle exhausts since the use of lead-containing petroleum products ceased in 2011.

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